

## **New Advances In The Investigation Of Photoinitiator Reactivity**

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### **Abstract**

In this paper a new approach was presented for the investigation of Photoinitiating Systems (PIS). Laser Induced PhotoAcoustic Calorimetry LIPAC was used to determine some important properties of PIS such as triplet quantum yields or triplet energy levels. Combined with the results obtained from molecular modeling at the ab-initio or density functional theory level, LIPAC allows the measurement of bond dissociation energy BDE of type I photoinitiators as well as their dissociation quantum yield.

### **Introduction**

Photoinduced radical polymerization reactions of a monomer (M) in the presence of a photoinitiating system (PIS) are largely encountered in the Radiation Curing area (e.g.[1,2]). The role of PISs was fully emphasized over the past three decades. The increase of the PIS efficiency lies on a practical approach requiring a lot of trials, a better knowledge of the excited state reactivity and a theoretical investigation of the processes involved.

The yield of the different primary reactions that occurs before the initiating step is governed by the photophysical and photochemical processes involved in the excited states, as very often presented: cleavage reactions, electron transfer reactions between the photoinitiator (PI) and amines, hydrogen abstraction reactions with hydrogen donors, quenching of triplet states by monomer, oxygen, light stabilizers or other additives, energy or electron transfer reactions, secondary reactions...

Most of the studies in this field are based on laser spectroscopies (e.g.[1-6]): time resolved photoconductivity [7], time resolved FTIR vibrational spectroscopy [8]. They bring about mechanistic information on the PIS - such as transient absorption spectra, lifetimes of excited states and rate constants of the various interaction reactions - and help to describe, from a kinetic point of view, the overall diagram of evolution of the excited states and reactive intermediates of PIS.

However, there is a lack of data about the energetics of the processes involved. This could be circumvented by the use of laser photothermal spectroscopies such as Time-Resolved Thermal Lens Spectroscopy (TRTLS) or Laser Induced PhotoAcoustic Calorimetry (LIPAC). These techniques allow the measurement of the heat produced in the medium, providing important kinetic and thermodynamic informations on the system studied. Many experimental data can be obtained, e.g. intersystem crossing quantum yields, triplet state energy levels, lifetimes, quantum yields of dissociation of cleavable photoinitiators, bond dissociation energies of amines used as coinitiator, formation enthalpies of the radicals, rate constants of interaction between the initiating radical and the monomer double bond, enthalpy of this addition reaction [9-10]...

Additionally, molecular modelling allows a new approach for the investigation of the reactivity of PIS: conformational and thermodynamical properties of ground state molecules, excited states, radicals as well as transition states become accessible. Combining both an experimental and a theoretical approach should improve the design of new PISs. This combined approach has been recently used for the investigation of e.g. i) the sensitization reactions which often occur in PIS (a proposed new model based on a thermal activation of the bond torsion [11,12] definitively explains the energy transfer in oxime derivatives usable as photobases in photoresist technology [13]), ii) the bond dissociation energy BDE of amines and the molecular factors that stabilize the aminoalkyl radicals [14] and governs their reactivity towards double bonds [15], iii) the quantum yields of dissociation and thermodynamical data such as the BDE or the enthalpy of the bond breaking reaction in cleavable PISs [10].

Such an approach will be exemplified in the present paper.

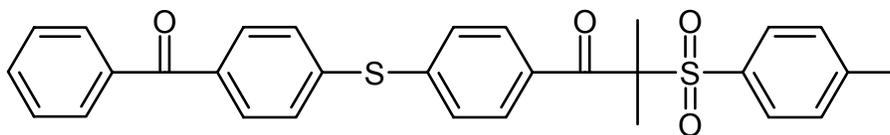
## Experimental

The experimental setup of the LIPAC was fully described elsewhere [9,14]. Briefly, the attenuated beam of a frequency tripled nanosecond Nd:YAG laser (Powerlite 9010, Continuum) irradiated a 1 cm cell equipped with a piezoelectric detector (Panametrics A609S 5MHz or A603S 1 MHz) through a 200 $\mu$ m or 500 $\mu$ m pinhole. The amplified signal was monitored by a transient digitizer (Tektronix 3052). The optical density of the samples was adjusted to 0.2 at the excitation wavelength (355nm). 2-hydroxybenzophenone (BPOH) was used as a calorimetric standard. Oxygen was removed by argon bubbling for 15 minutes.

All quantum calculations were carried out using the Gaussian 98W suite of programs. We selected the B3LYP hybrid parameterization with 6-31+G(d) or 6-311++G\*\* basis sets.

## Procedure

Excitation of molecules in solution results in the creation of excited states that are doomed to deactivate or react. Photophysical deactivations occurring through non-radiative processes and exothermic photochemical reactions both release heat in solution. This temperature jump causes a change of pressure that generates propagating acoustic waves through the media. This is directly related to the heat evolved and consequently to the photochemistry of the system studied. The high frequency component of this acoustic wave, that corresponds to the fast photochemical processes, is directly monitored by Laser Induced Photoacoustic Calorimetry and therefore, the heat released from states deactivating faster than 20-100 ns gives a detectable signal. Figure 1 shows a typical signal obtained by LIPAC in the case of 2-hydroxybenzophenone (BPOH) and the bifunctional photoinitiator Esacure 1001 (Lamberti Spa., Scheme 1) [16-17] in acetonitrile and under argon.



**Scheme 1: Chemical structure of Esacure 1001.**

As can be seen, the amplitude of the acoustic wave corresponding to Esacure 1001 is lower than that of BPOH. The latter is known to release the whole excitation energy in solution in less than 1 ns, and therefore is used as a calorimetric reference. On the contrary, Esacure

1001 gives rise to a triplet state that deactivates slowly in solution, and therefore the fast heat release results in a lower acoustic wave.

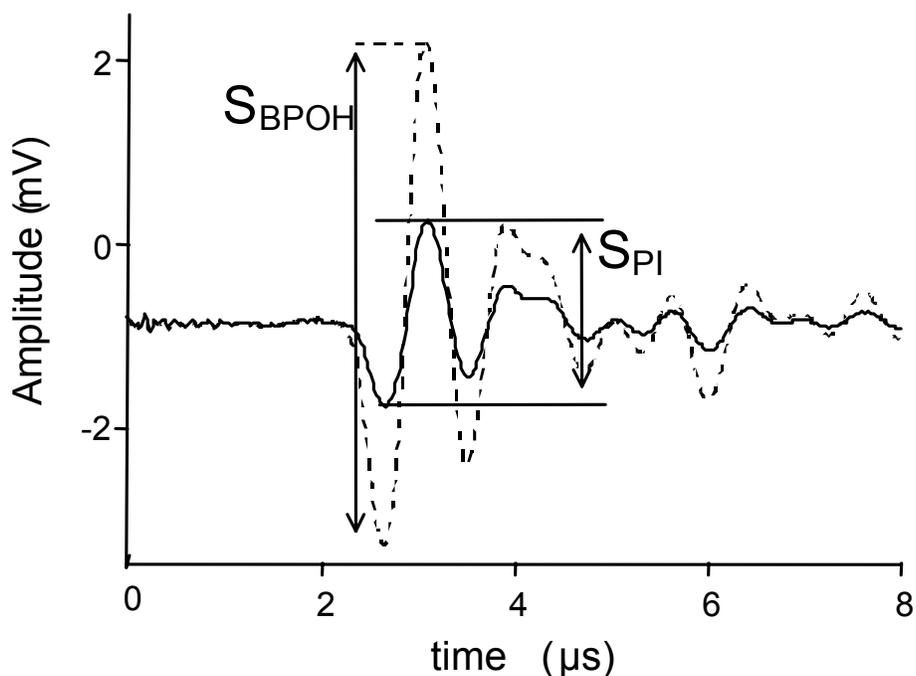


Figure 1: Typical LIPAC signals obtained in the case of BPOH and Esacure 1001 as PI in acetonitrile under argon.

The values of the signal corresponding to the reference ( $S_{BPOH}$ ) and the photoinitiator ( $S_{PI}$ ) are related to the energy level  $E_T$  and the quantum yield  $\phi_T$  of the PI triplet state through the following equation [9]:

$$\phi_T \cdot E_T = h\nu \cdot \left(1 - \frac{S_{PI}}{S_{BPOH}}\right) \quad (1)$$

If the triplet energy of the photoinitiator is not known, an energy transfer experiment monitored by LIPAC can provide a good estimate. In that case, the excited photoinitiator must be totally quenched by a well characterized energy acceptor A according to:

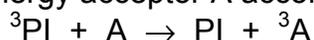


Table 1. Triplet quantum yield of different photoinitiators measured by LIPAC.

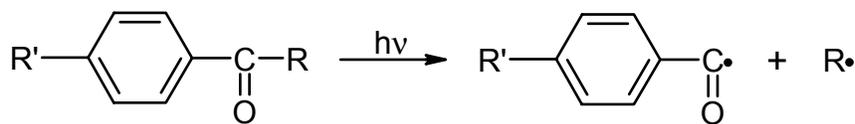
Photoinitiator	Solvent	$\phi_T$	literature
Benzophenon	Acetonitrile	0.98±0.02	1.0 [18]
Esacure 1001	Acetonitrile	0.78±0.02	0.7 [16]
Benzil	Benzene	1.00±0.02	0.92 [18]
Michler ketone	Benzene	0.95±0.02	0.91 [18]

The amount of the acceptor triplet state depends directly on the  $\phi_T$  of PI and then, the slow heat release corresponds to the triplet state of A. Knowing the triplet energy of this acceptor, it is quite easy to retrieve  $\phi_T$ . The latter value can be used in Eq. 1 to deduce  $E_T$ . In the case of Esacure 1001  $\phi_T=0.78$ , in good agreement with the value of 0.7 determined by energy transfer experiments [16].

This procedure can be applied to different photoinitiators. The results obtained as shown in Table 1 are in very good agreement with the literature values.

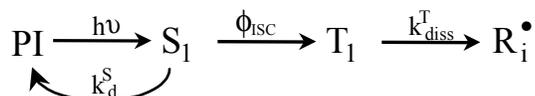
### Cleavage process in commercially available photoinitiators

Acetophenone derivatives represent a widely used family of commercially available photoinitiators. The cleavage process lead to a direct formation of two radicals from the excited state (Scheme 2). As the triplet state formation is very fast, the cleavage process occurs mainly in the triplet state [2,33]. These radicals can initiate the polymerization reaction through an addition reaction to the monomer double bond.



**Scheme 2: photodissociation process of acetophenone derivatives**

The photochemical reactivity is governed by the quantum yield of dissociation  $\phi_{\text{diss}}$  which depends on the different deactivation pathways of the excited states (Scheme 3).

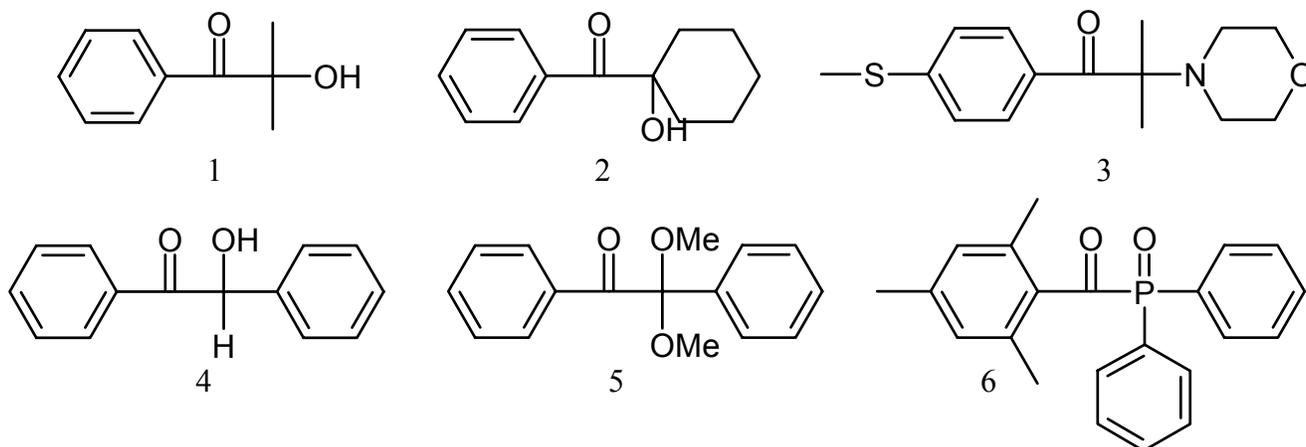


**Scheme 3: mechanism for the photocleavage process.**

The evaluation of  $\phi_{\text{diss}}$  is a difficult task: there was not a great deal of studies in this field and surprisingly, the factors controlling the photodissociation in the triplet state of large organic molecules remain unclear. Classical methods to evaluate  $\phi_{\text{diss}}$  were only operative in very few examples and were difficult to use.

The common idea states that the bond dissociation enthalpy (BDE) of the bond being broken should play a crucial role, but there is no direct evidence that this factor alone governs the dissociation efficiency. The combined use of photothermal techniques and molecular modeling should lead with a limited number of assumptions to both quantum yields of dissociation and thermodynamical data such as BDE or the photocleavage reaction enthalpy  $\Delta H_r$ .

Eight cleavable photoinitiators (obtained from Ciba Specialties) belonging to well-known structures have been selected (Scheme 4) : acetophenone derivatives (1, 2), morpholino ketone derivatives (3), benzoin (4), 2,2-dimethoxy-2-phenyl-acetophenone (5), and a phosphine oxide derivative (6).



**Scheme 4: Type I photoinitiators studied.**

During the cleavage process, some heat is released in the media ( $E_{rel}$ ) that could be monitored by LIPAC. This energy  $E_{rel}$  corresponds to both the heat evolved during the dissociation process for the molecules that react and the heat of deactivation from the excited state to the ground state for the excited molecules that do not dissociate. Therefore, the difference between the energy of the incident photon and the heat monitored by LIPAC is equal to the quantum yield of dissociation times the bond dissociation energy (BDE) of the compound [10]:

$$h\nu - E_{rel} = \phi_{diss} \text{ BDE} \quad (2)$$

From Table 2, it can be seen that the corresponding values for the photoinitiators 1-6 vary strongly. This could be ascribed mainly to the differences in the dissociation quantum yields.

**Table 2. Triplet Energy  $E_T$ , data from LIPAC, bond dissociation energy BDE and dissociation quantum yield for the different photoinitiators 1-6.**

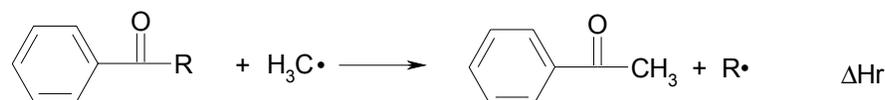
PI	$E_T$ (kcal/mol)	$\phi_{diss} \times \text{BDE}$	BDE <sup>a</sup> (kcal/mol)	$\phi_{diss}$	$\phi_{diss}^c$
9	71.4	51	65.0	0.8	0.38
10	66.8	53	63.5	0.8	1.0
11	61	18	56.8 <sup>b</sup>	0.3	0.13
12	72.2	29	60.0	0.5	0.35
13	66.2	49	50.9	0.95	1.0/0.52
14	62.6	41	57	0.7	0.5/0.8

a) evaluated with eq 2. b) calculated as the difference between the energy of the radicals and that of the ground state. c) see Ref. 10.

In order to retrieve the values of  $\phi_{diss}$ , one have to estimate the BDE. This could be calculated with a good precision by using molecular modeling at the ab-initio or density functional theory level.

One of the best methods estimates the BDE from the calculation of the different energy

terms of a so-called isodesmic reaction such as :



**Scheme 6: isodesmic reaction**

In this method, the error introduced by the computation are counterbalanced and the experimental BDE value of acetophenone is introduced as a reference. The BDE of the photoinitiator PI is then calculated from (3). The results are gathered in Table 2, as well as the values of the quantum yields of dissociation.

$$\text{BDE}_{\text{PI}} = \text{BDE}_{\text{acetophenone}} + \Delta H_r \quad (3)$$

The agreement between our results and the values available from the literature is quite good. Interestingly, it should be noted that the literature values are often lower than the present results. This is attributable to the technique used for the measurements. Indeed, one of the classical technique used for the evaluation of dissociation quantum yields consists in carrying out the photolysis of the compound under a continuous light, and following the PI bleaching by absorption spectroscopy. However, this procedure suffers from the presence of recombination second-order reactions of the radicals after the cleavage process: this contributes to the recovery of the PI ground state and thereby decreases the photolysis efficiency. In contrast, the method employed in this paper measures the dissociation heat just after the reaction: this technique is not sensitive to the possible second-order recombination. Consequently, it is not surprising that the quantum yields obtained from photolysis are lower than our values. To our opinion, the LIPAC method described in this paper is more appropriate to the study of the intrinsic reactivity of photoinitiators.

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